

Headspace analysis of solvents in cocaine and heroin samples

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Solid phase adsorption of headspace vapours was used to trap occluded solvent residues contained in 41 heroin and 54 cocaine samples, seized in Switzerland between 1994 and 1996, onto activated charcoal. The residues were eluted with carbon disulphide and analysed by GC-FID. Identification was confirmed by GC-MS. The detection limits between 2–15 ppm were determined empirically on a w/w basis for 250–300 mg powder samples. Twelve and 16 solvents were identified in the heroin and cocaine samples respectively. It was possible to relate cocaine samples to each other, but heroin comparisons proved more problematical. Trends and geographic variation in solvent use are considered, and recommendations are made with respect to the control of certain solvents frequently encountered in heroin and cocaine samples.

Le principe de l'adsorption sur phase solide de vapeurs headspace a été utilisé afin de collecter sur du charbon actif des résidus de solvants contenus dans 41 échantillons d'héroïne et 54 de cocaïne, saisis en Suisse entre 1994 et 1996. Les résidus ont été élués à l'aide de disulfure de carbone et analysés par GC-FID. L'identification a été confirmée par GC-MS. Les limites de détection, déterminées empiriquement, sont de 2–15 ppm p/p pour des échantillons de poudre de 250–300 mg. Douze et seize solvants ont été identifiés dans les échantillons d'héroïne respectivement de cocaïne. Il a été possible de relier des échantillons de cocaïne entre eux, mais les comparaisons pour l'héroïne se sont montrées problématiques. Les variations géographiques et les différentes tendances dans l'utilisation des solvants ont été considérées, et des recommandations sont faites au sujet du contrôle de certains solvants fréquemment retrouvés dans les échantillons d'héroïne et de cocaïne.

Die Festphasenadsorption aus dem Dampfraum wurde benutzt, um die eingeschlossenen Lösungsmittelrückstände von 41 Heroin- und 54 Cocainproben auf Aktivkohle zu sammeln. Die Proben sind in der Zeit von 1994 bis 1996 in der Schweiz sichergestellt worden. Die Rückstände wurden mit Schwefelkohlenstoff eluiert und mit Hilfe der GC-FID analysiert. Die Identifizierung ist mittels GC-MS abgesichert worden. Die Nachweisgrenze von 2–15 ppm wurde empirisch auf Gewichtsbasis an 250–300 mg der pulverisierten Proben bestimmt. In den Heroinproben wurden 12, in den Cocainproben 16 Lösungsmittel identifiziert. Während Cocainproben einander zugeordnet werden konnten, waren Vergleiche bei Heroin problematisch. Trends und geographische Unterschiede beim Gebrauch der Lösungsmittel werden betrachtet und Vorschläge zur Kontrolle ganz bestimmter, in Heroin- und Cocainproben häufig auftretender Lösungsmittel gemacht.

Se utilizó la absorción en fase sólida de vapores de espacio de cabeza para atrapar en carbon activo los residuos de disolventes contenidos en 41 muestras de heroína y 54 de cocaína, aprehendidas en Suiza entre 1994 y 1996. Los residuos se eluyeron con sulfuro de carbono y se analizaron por GC-MS. Los límites de detección entre 2 y 15 ppm se determinaron empíricamente sobre una base peso/peso para 250–30 mg de muestra en polvo. Se identificaron 12 y 16 disolventes en heroína y cocaína respectivamente. Fue posible relacionar entre sí las muestras de cocaína pero esto fue más problemático en las de heroína. Se hacen consideraciones sobre tendencias y variaciones geográficas en el uso de disolventes y se hacen recomendaciones respecto al control de determinados disolventes que se encuentran con frecuencia en las muestras de heroína y cocaína.

Key Words: Forensic science; Drugs of abuse; Heroin; Cocaine; Drug profiling; Solvent residues.

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Introduction

There are both national and international legislative measures for the control of drugs of abuse, and also for the compounds employed for their extraction, synthesis and purification. Of particular international significance were the United Nations publications in 1961, 1971 and 1988 [1–3]. Article 12 of the latter declared that certain precursor chemicals employed in the synthesis of drugs of abuse should come under international control. Since the 1988 convention, the total number of seizures of the listed chemicals has declined, but increasingly, new alternatives have been sought and found for use in clandestine laboratory operations. In addition to the precursor chemicals, solvents are required for the synthetic reactions and subsequent purification stages of the drugs. Under the 1988 convention, acetone and diethylether were listed as solvents which should come under control, or at least observation.

Cocaine is derived from the extract of the plant *Erythroxylon coca* L. [4]. A large number of solvents are known to be utilised for the extraction, reaction sequences and final purification steps of the cocaine hydrochloride salt, the dose form most frequently encountered in Switzerland. Heroin (containing diamorphine) is derived from the latex of *Papaver somniferum* L. [5], and again a number of steps are required to purify the final product. It is possible to detect the solvent residues from these steps in drug samples [6–8] and the data obtained has been used to complement other comparative studies including the use of TLC, GC-MS, HPLC and metal analysis using FAAS [9].

This paper reports on the solvent residues contained within heroin and cocaine samples, seized in Switzerland between 1994 and 1996. The profiles of solvents are given, and comparison is made between samples, using traditional GC studies and analysis of the solvent profiles. The frequency of occurrence of different solvents and the geographical variation in solvent use are discussed.

Materials and methods

Drug samples and reagents

Samples of cocaine hydrochloride (54) and heroin base (41) were obtained from customs and excise and police officers from cities in the Jura and Ticino cantons in Switzerland during the period 1994–1996. All chemicals and reagents were of analytical reagent grade or better and were obtained from Fluka AG, Switzerland.

Headspace trapping of solvent residues from drug samples

The solvent residues were trapped using static headspace trapping onto activated charcoal, using a method modified from the analysis of arson accelerant debris [10]. The powdered drug (250–300 mg) was placed in a GC derivatisation vial. A 0.25 ml insert, containing a small piece (0.1 g) of activated charcoal strip (DFLEX®) was added. The vial was then sealed and the contents were heated to 80°C for 60

minutes and allowed to cool. The solvents, adsorbed onto the activated charcoal strip were eluted with 50 µl CS₂ and 1 µl CS₂ eluate analysed.

In order to verify that the method was applicable, a similar technique was employed for the analysis of a standard mixture of solvents. A standard mixture of 19 solvents namely, acetaldehyde, methanol, ethanol, acetone, isopropanol, diethylether, dichloromethane, methylacetate, methyl-ethylketone, ethylacetate, hexane, chloroform, isobutanol, methylisobutylketone, toluene, m-xylene, p-xylene, o-xylene and 1,2,3-trimethylbenzene was prepared in carbon disulphide, at a concentration of approximately 2 µl/ml, except for toluene, m-xylene, p-xylene, o-xylene and 1,2,3-trimethylbenzene which were prepared at 1 µl/ml. The internal standard, n-decane, was added at 1 µl/ml. An aliquot of the mixture, ranging in size from 0.05 to 5 µl was placed on potato flour (250–300 mg), and the solvents were trapped as for the drug samples. Blanks were also prepared, using all of the same materials, but excluding both drugs and solvents.

Gas chromatography

Gas chromatography was carried out for each of the solvents alone, and as a mixture, to determine retention times. A Perkin Elmer 8500 series gas chromatograph was employed, fitted with a DB-1 column (60 m x 0.33 mm i.d., 3 µm layer thickness), operated with helium as the carrier gas (column pressure 17 psig, 0.7 ml/min). The injection and FID temperatures were 280°C, the injection being made with a split ratio of 1:30. The temperature programme was started at 35°C, holding for 14 min, rising at 5°C/min to 100°C, then rising at 7°C/min to 245°C and holding at this temperature. The temperature programme was terminated at this point, unless petrol was detected, in which case the temperature of the column was held at 245°C for ten minutes. Detection was by flame ionisation. Relative retention times were calculated against the retention time of the internal standard, n-decane, for the standards, and the solvents were identified by comparison of their relative retention time against n-decane with these data. Carbon disulphide blanks were analysed between each sample to demonstrate that carry over had not occurred.

Stability of the GC system

The stability of the GC system described for the analysis of the solvents, was tested within day and between different days. Three analyses were made on each of three days giving nine analyses in total and the relative retention times were calculated. The Kruskal Wallis test [11] was used to determine whether there were significant differences between analyses.

Limits of detection

Known masses (calculated from the volume of the liquid applied and the density) of solvents were placed on the

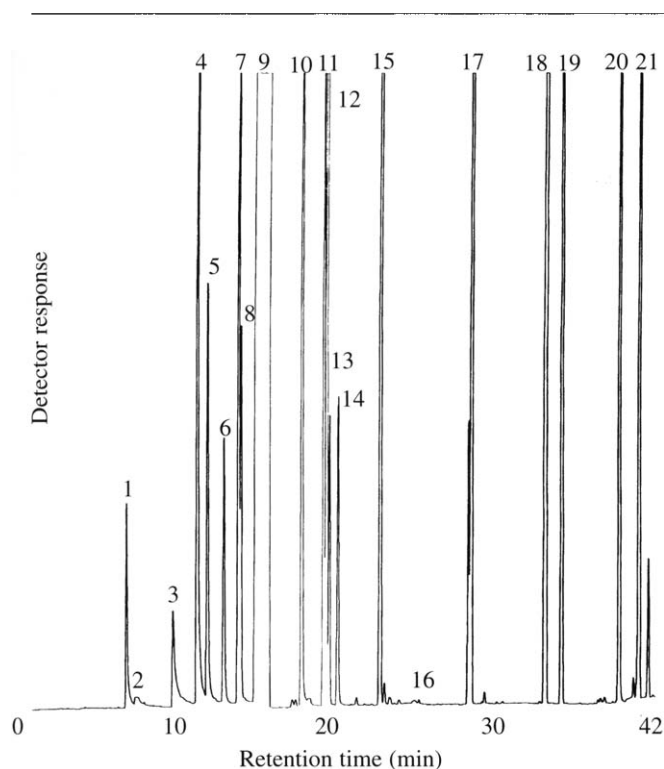


FIGURE 1 Chromatogram of solvent standards identified in cocaine and heroin samples in this study. Elution order: 1, acetaldehyde; 2, methanol; 3, ethanol; 4, acetone; 5, isopropanol; 6, diethylether; 7, dichloromethane; 8, methylacetate; 9, carbon disulphide; 10, methylethylketone; 11, ethylacetate; 12, hexane; 13, chloroform; 14, butanol; 15, benzene (from carbon disulphide); 16, methylisobutylketone; 17, toluene; 18, m & p-xylene; 19, o-xylene; 20, n-decane (internal standard); 21, 1,2,3-trimethylbenzene.

potato flour and treated as for the drug samples. The lowest mass of solvent which could be detected in the gas chromatogram was determined, empirically, to be the detection limit.

Results and discussion

The separation of the solvents that was achieved is illustrated in Figure 1. All of the solvents of interest could be resolved to baseline in 42 minutes. The identification of each compound was confirmed using GC-MS (operating conditions as for GC-FID). The Kruskal Wallis test demonstrated that there was no significant difference ($p < 0.05$) between analyses. A small amount of benzene was observed in the carbon disulphide, but no other solvents were observed in the blank samples. When the presence of benzene was suspected in the sample, CS_2 from Aldrich (benzene-free but with other impurities, acetone and diethylether) was used for elution of the solvents from the charcoal strip. In this way, use of two CS_2 samples allowed detection of benzene, acetone and diethylether. The relative retention times of each of the compounds is given in Table 1.

TABLE 1 Retention time data for the solvents detected and employed in this study.

Solvent	Retention time (min)	Relative retention time
Formaldehyde	5.0	0.32
Acetaldehyde	7.0	0.45
Methanol	7.6	0.49
Ethanol	10.0	0.64
Acetone	11.6	0.74
Isopropanol	12.4	0.79
Diethylether	13.2	0.85
Dichloromethane	14.0	0.90
Methylacetate	14.2	0.91
Carbon disulphide	15.6	1.00
Methylethylketone	18.0	1.15
Ethylacetate	19.2	1.23
Hexane	19.4	1.24
Chloroform	19.6	1.26
2-butanol	20.2	1.29
Benzene	22.8	1.46
Methylisobutylketone	25.2	1.62
Toluene	28.4	1.82
M,p-xylene	33.0	2.12
O-xylene	34.2	2.19
N-decane	37.6	2.41
1,2,3-trimethylbenzene	39.0	2.50

The solvents identified in the cocaine hydrochloride and heroin hydrochloride samples are given in Tables 2 and 3 respectively. Of the cocaine samples, two pairs were found to match. Samples 95/90.2 and 95/90.3 were from the same seizure. The chromatograms of the solvents that they contained are shown (Figure 2), as are the chromatograms of their adulterants and diluents (Figure 3). Cocaine samples 105 and 106 were from different seizures, but identified as being related from their solvent residue composition and their adulterants and diluents (Chromatographic operating conditions are omitted for brevity but are available from the authors).

The occluded solvent composition of several heroin samples matched (for example, samples 95/11.B., 95/276, 95/877.1c) but the impurity profiles did not, indicating that whilst the same solvents may have been used, it was unlikely that the samples did come from one larger batch at an earlier date. This occurred with toluene and methylethylketone (MEK) and toluene and dichloromethane as solvent pairs. This suggests that at least three solvents are required before a match can be called and that toluene, dichloromethane and MEK are not good profiling markers for solvent comparison.

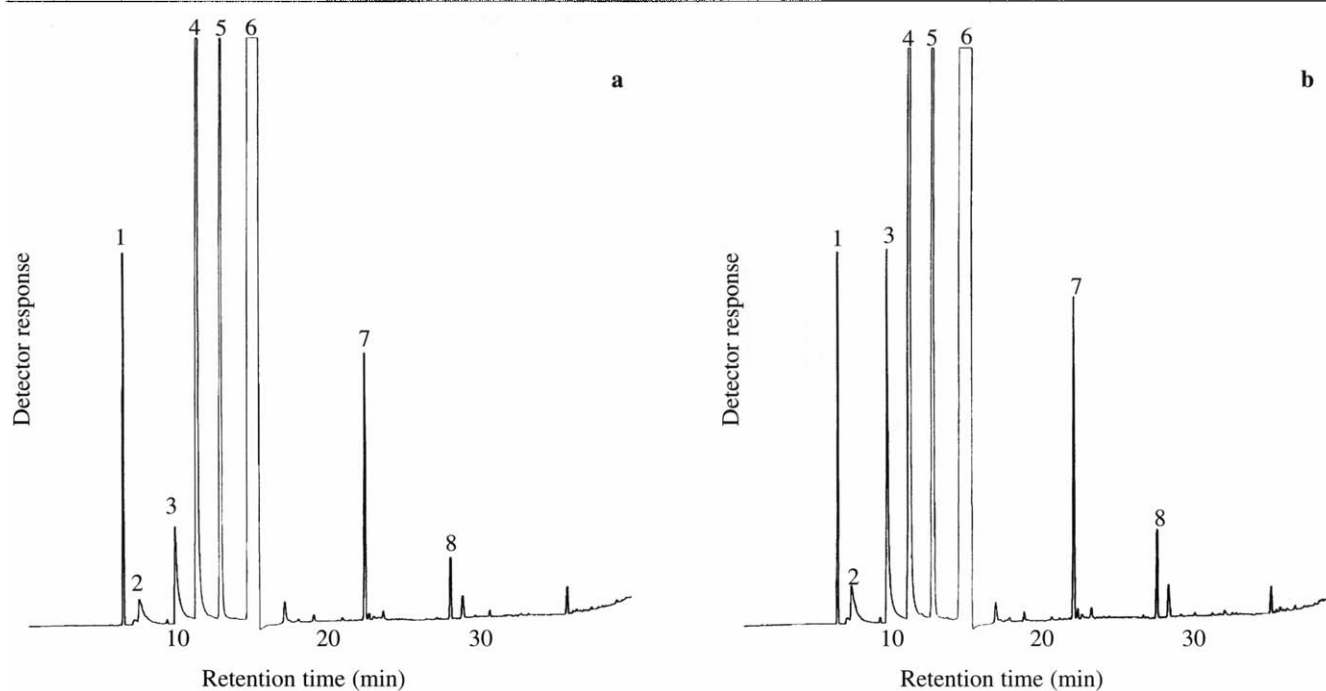


FIGURE 2 Occluded solvents identified in cocaine samples (a) 95/90.2; (b) 95/90.3. 1: chloroform; 2: methanol; 3: ethanol; 4: acetone; 5: diethylether; 6: carbon disulphide; 7: benzene (from carbon disulphide); 8: m and p-xylene.

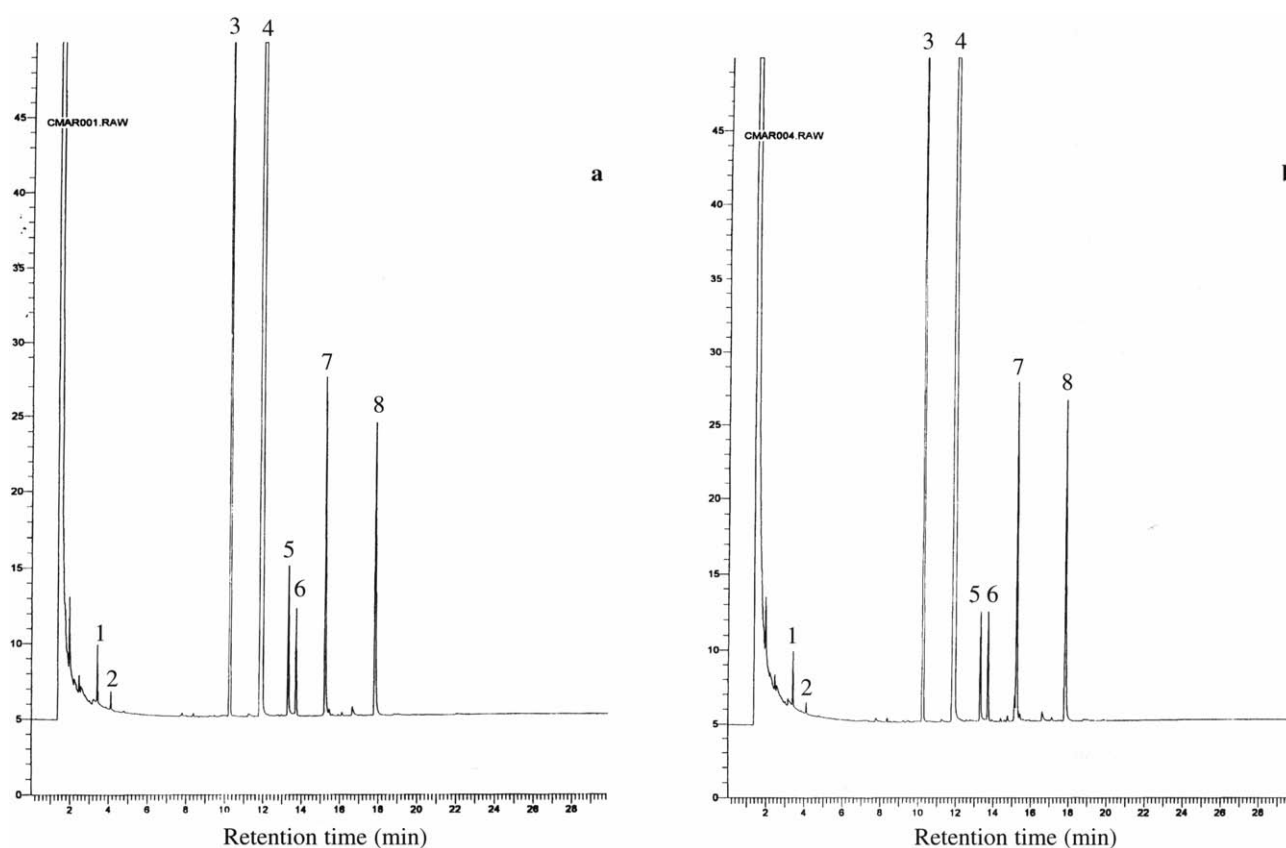


FIGURE 3 Impurities found in cocaine samples (a) 95/90.2; (b) 95/90.3. 1: ecgonine methyl ester-TMS; 2: ecgonine-TMS; 3: heneicosane (internal standard); 4: cocaine; 5: benzoylecgonine-TMS ; 6: norcocaine-TMS; 7: cis-cinnamoylecgonine methyl ester-TMS; 8: trans-cinnamoylecgonine methyl ester-TMS.

TABLE 2 Occluded solvents identified in cocaine in this study.

Sample	Solvent Number																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
86	*				*		*									*			
127																			
131	*																		
168	*																		
169	*																		
173																			
184																			
185	*																		
195																			
196																			*
4863																			
105	*				*		*	*		*									*
106	*				*		*	*		*									*
17.1A	*				*		*			*			*						*
343.2B	*				*														*
62.9D																			
7A.2																			
95/12.A	*		*							*									
95/13.10	*					*							*				*		
95/15.1	*																		
95/206	*				*	*		*					*		*	*			
95/22																			
95/23.20S																			
95/23.23	*																		
95/91.1	*		*								*			*					
96/19.3	*				*	*	*	*		*			*	*	*	*	*	*	*
95/209	*				*	*	*	*		*			*		*	*	*	*	*
95/245	*				*	*	*	*		*	*				*	*	*	*	*
95/2538	*	*			*	*	*	*		*	*				*	*	*	*	*
95/264	*				*	*	*	*		*	*				*	*	*	*	*
95/285	*				*	*	*	*		*	*				*	*	*	*	*
95/247																			
95/372																			
95/374	*																		
95/409	*				*		*			*						*			*
95/462	*				*		*	*			*			*	*	*	*	*	*
95/524					*														
95/54	*				*	*	*	*		*						*	*	*	*
95/75	*																		
95/73.3													*						
95/8.A	*							*		*						*			
95/840.1	*																		
95/850.2	*									*	*								
95/86.3	*		*	*	*		*			*	*			*		*			
95/89.1	*				*					*	*							*	
95/90.2	*		*	*	*		*									*			
95/90.3	*		*	*	*		*									*			
95/90.4		*														*			
96/214	*		*				*	*											
96/216.2					*	*	*								*	*			
96/220	*		*		*											*			*
96/225.1	*				*		*												
C3.D	*																		
kho 15	*				*		*												

* Solvent present

1: chloromethane; 2: acetaldehyde; 3: methanol; 4: ethanol; 5: acetone; 6: isopropanol;
 7: diethylether; 8: dichloromethane; 9: methylacetate; 10: methylethylketone; 11: ethylacetate;
 12: hexane; 13: chloroform; 14: isobutanol; 15: methylisobutylketone; 16: toluene;
 17: m and p-xylene; 18: o-xylene; 19: 1,2,3 trimethylbenzene.

TABLE 3 Occluded solvents identified in heroin in this study.

Sample	Solvent Number																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
95/11.B								*					*						
95/224								*					*	*	*	*			
95/276								*					*						
95/277								*					*						
95/286						*							*	*	*	*			
95/302													*						
95/308													*						
95/4862.4													*						
95/50								*											
95/593		*				*							*						
95/602		*											*						
95/79													*						
95/82.1													*						
95/840.2B													*						
95/841.1a			*		*	*		*	*			*	*	*	*	*			
95/841.1A								*					*						
95/842.1													*						
95/843.1a													*						
95/844.1													*						
95/846.1b													*						
95/848.1						*							*						
95/849.1													*						
95/85.1						*		*					*						
95/850.1c									*				*						
95/856.1B													*						
95/859.1a													*						
95/866.1		*				*							*						
95/872													*						
95/875.1						*							*						
95/877.1c								*					*						
95/89.2													*						
95/9.4						*							*						
95/9.B													*						
96/0001.2													*						
96/0007.1													*						
96/0171.3													*						
96/13.1													*						
96/3.2													*						
96/4.1													*						
96/7.1		*				*		*					*						
96/9.1						*		*					*						

* Solvent present

1: acetaldehyde; 2: ethanol; 3: acetone; 4: isopropanol; 5: diethylether;
6: dichloromethane; 7: methylacetate; 8: methylethylketone; 9: ethylacetate; 10: hexane;
11: chloroform; 12: isobutanol; 13: toluene; 14: m & p-xylene; 15: o-xylene;
16: 1,2,3 trimethylbenzene.

The frequency of occurrence of the solvents is given in Table 4. The greatest variety of solvents was encountered in the cocaine samples. This perhaps reflects the more complex nature of the extraction and subsequent synthetic and purification process employed for the production of cocaine, relative to that of heroin, and is in agreement with previously published data [8,12]. Of the solvents found in cocaine, only the two most common were listed under article 12 of the Convention on Illicit Traffic, 1988. Of the solvents encountered in heroin, none are listed. Clearly, some solvents such as petrol will never be subject to regulation.

However, whilst some large volume shipments of solvents are monitored by law enforcement agencies, perhaps greater attention should be paid to the shipment of large volumes of common solvents such as toluene, methylethylketone, ethyl acetate and methylisobutylketone.

Examination of Table 4 in conjunction with previous studies [8,12] indicates that there are some regional variations in the solvents contained in the drug samples. With respect to cocaine, a greater number of solvents were encountered in Swiss samples than in either US or Canadian material.

TABLE 4 Occluded solvents identified in this study and previously reported [8,12] as percentage frequency in the samples.

Solvent	Drug sample				
	Swiss Cocaine	Swiss Heroin	Canadian Cocaine	US Cocaine	US Heroin
Toluene	46.3	71.4	7.4	59.0	25.0
Acetone	44.4	0.0	62.5	52.0	57.0
Diethylether	37.1	0.0	62.5	52.0	57.0
Methylethylketone	24.1	19.1	54.5	65.0	25.0
Isopropanol	16.6	0.0	0.0	0.0	5.0
Dichloromethane	16.6	21.4	2.8	41.0	0.0
Methanol	12.9	0.0	0.0	0.0	0.0
Chloroform	11.1	0.0	0.0	0.0	0.0
Isobutanol	7.4	0.0	0.0	0.0	0.0
Ethanol	5.6	0.0	0.0	0.0	0.0
Acetaldehyde	3.7	9.5	0.0	0.0	0.0
Benzene	0.0	0.0	11.4	55.0	0.0
Hexane	0.0	0.0	0.0	61.0	3.0
Xylene	0.0	0.0	0.0	31.0	19.0
Cyclohexane	0.0	0.0	0.0	27.0	0.0
Methylacetate	0.0	0.0	0.0	0.0	3.0

Further, hexanes and aromatics were common in US cocaine, whilst they were rare in Swiss cocaine, with the exception of toluene. There was less variation with respect to the heroin, although in the US some solvents, such as ethylacetate, acetone and diethylether, were common, whilst they were rare or absent in Swiss heroin. The examination of solvents may shed some light on the geographical origin of a sample, and a large amount of material is not required.

The analysis of solvents was introduced in a logical sequence of tests used in drug profiling in our laboratory, providing a simple and independent means of confirming links from organic impurity and inorganic ion determinations. As previously suggested [6,7], in this technique, once the solvents have been trapped, the drug sample remains intact. In this laboratory, and in other studies [8], it has been found that analyses of the solvents may be carried out on samples up to two years old, and provides valuable additional information in the comparison of drug samples.

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